Thermal Response of Explosives Systems

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Abstract
Several years ago, we began an effort to understand the thermal response of explosive systems, especially reaction violence and what controls it. We have conducted several different types of experiments in order to generate quantitative data as well as a qualitative description of the relevant processes. All of our experiments have been conducted with the HMX based explosive, PBX 9501. Small scale experiments were conducted to determine the thermal profiles, time, and location of ignition as a function of heating rate. Other small scale experiments were conducted to give a visual picture of processes that occur in the explosive after ignition. Large scale experiments with cylindrical liners were conducted to provide temperature, time, and location of ignition data for selected heating rates and to relate liner collapse velocities to the reaction violence associated with the selected heating rates. Kinetics experiments and modeling have been conducted to provide a description of temperature, time, and location of ignition as a function of heating rates.

Introduction

When we began this study about three years ago, it was painfully obvious that we did not have a sufficiently good understanding of the behavior of explosives containing

munitions in extreme thermal environments to give responsible answers to questions raised in accident scenario analyses. We were aware of various behavior trends: Cookoff violence increases with increased charge size, with increased confinement, and with decreased rate of heating. In addition, geometry can affect cookoff violence and, of course, cookoff violence can be quite sensitive to explosive formulation parameters. Thermal explosion theory could be used to predict temperature at which a runaway thermal excursion would occur for a given thermal boundary condition. More complex chemical kinetic models could be used to predict time to thermal runaway. It turned out that available kinetic models were inadequate to predict ignition location. However, at the time, there were no data regarding ignition location against which to compare the models. There was not (and still isn't) a capability for predicting reaction violence.

We believe that a good measure of our understanding of cookoff behavior is how well we can answer the following questions:

1. At what temperature, time, and location does ignition occur? The importance of being able to predict time and temperature of ignition to analysis of accident scenarios is obvious. At the time we began our effort, we believed ignition location strongly influenced reaction violence. Since then, we have realized that other factors, such as the steepness of the thermal gradient, and the amount of material that has reached or exceeded a threshold temperature also track with ignition location. Further work is required to determine which factors are most important in controlling reaction violence. However, measurements of ignition location provided important additional constraints upon chemical kinetic/thermal conduction models.
2. How does reaction spread? We view cookoff violence as a competition between the energy release rate resulting from spread of reaction and the process of case expansion and failure. Case failure allows pressure venting, and escape of hot reaction products from direct contact with unreacted material. It thus provides a quenching mechanism. While this presents an enticing perspective, it is clear that accurate modeling capability will require experimental evidence to allow cataloging of all (potentially competing) mechanisms and accurate data against which to compare mathematical models.
3. What is the case expansion rate? Case expansion rate (or, in the case of a shaped charge device, liner collapse rate) provides a quantitative measure of reaction violence and the history of energy release prior to case failure. Case expansion rate and liner collapse rate are thus valuable data sets against which to judge a model. Of course, they are of practical interest in analysis of accident scenarios as well, where fragment (or jet) lethality is often an issue.
4. What fraction of the material reacts after case failure and contributes to airblast? Of course, we are interested in how much reacts prior to case failure, as that will influence case expansion rate and liner collapse rate. However, it is important to remember that pieces of explosive reacting in the fireball after case failure will contribute to the airblast, and thus are important for analysis of internal blast damage, and near and far-field external blast damage.
5. How repeatable are the experiments? Ultimately, we seek the capability to define the boundary between "safe" and "unsafe" for various measures of safety, and to locate

the results of various accident scenarios with respect to that multi-dimensional boundary. In addition, we want to assign some margin of safety. We would like that margin to be accurate, and well defined. This requires that we have good statistics regarding the repeatability of the events of interest.

6. How do the answers depend upon heating rate and other parameters? Of course, a good model must include all the important parameter effects and all the important mechanisms in a quantitative fashion. In safety, a frequent (often fatal) error is the use of an analysis that treats one mechanism well, but excludes others, or applies that one mechanism in a domain where it has not been validated.

Small Scale Radial Cookoff Experiments

We have been conducting cookoff experiments using small scale cylindrical charges of PBX 9501. The experiments were instrumented with thermocouples located in the central plane of the charge (see Figure 1). Heating tape was used to provide a controlled temperature boundary condition. The charges were lightly confined. (Early experiments were confined by 1/16" copper sleeves. Later ones were confined with 1/4 inch copper sleeves.) The purpose of these particular experiments was to obtain temperature histories as a function of position and externally imposed heating. These experiments provided data on ignition location and were very valuable in checking chemical kinetic models.

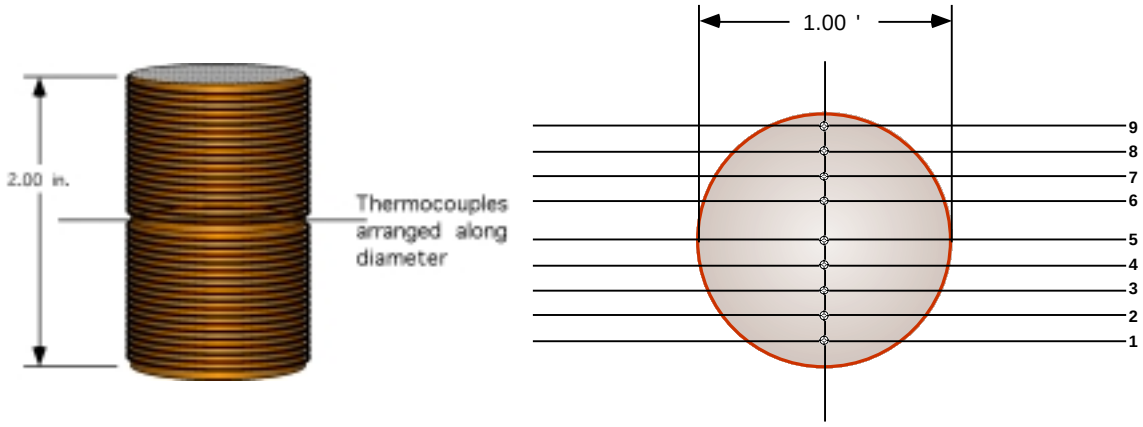

Figure 1: Schematic of small scale radial cookoff experiment.

The temperature time curves for one such experiment are shown in Figure 2. In this particular shot, the thermocouples 1-9 are in the explosive. Thermocouple traces 11 & 12 were at the HE/casing interface, and 10 measured the ambient air temperature. Considerable care was taken to insure radial symmetry on the boundary. Care was also taken to insure that the two ends of the charges were always cooler than the plane where

the thermocouples were placed. This was to insure that any reaction effects (such as ignition!) would occur first in the measurement plane.

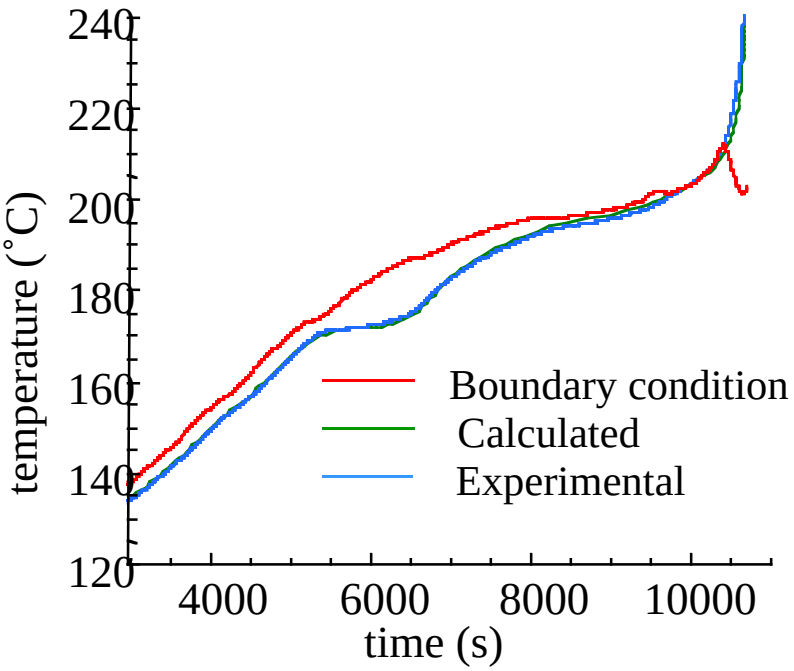

Figure 2: Thermocouple traces from one of the radial cookoff experiments. For clarity, only one experimental trace, one calculated trace, and the boundary trace are shown. However, the agreement between calculated and experimental values was equally good for all traces.

As the temperature of the boundary was raised, a temperature gradient developed, with the temperature of the inside of the charge lagging that of the boundary. At about 165 C, (in this particular experimental configuration) the thermocouple data showed a flattening in their slope, that persisted for a short length of time. This was a result of the HMX in the PBX 9501 undergoing a transition from the β to δ phase (1). The phase change is endothermic, and the absorption of heat causes the flattening of the temperature trajectory. Once the material was all converted to δ phase, the temperature traces resumed their upward climb. Note that the phase change occurred earliest in the material nearest the boundary. This is simply because it reached the transition temperature first. Note also that all of the material was converted to the δ phase prior to the sharp upturn in the thermocouple traces. There is about a seven per cent volume increase associated with the β to δ phase transition. This results in significant crystal fracture and the introduction of microporosity. Both of these are believed to sensitize the material to impact or shock loading. Since the last step in the transition to detonation is formation of a shock wave, the phase transition may play an important role in determining reaction violence. The

rapid increase in slope of some of the thermocouples results from exothermic reactions occurring. In this particular instance, the runaway reaction occurred at the center of the charge. More rapid heating rates at the boundary would drive the ignition location away from the center.

We attempted to model the temperature traces for this and other similar experiments, using the best available chemical kinetics model, that of Tarver and McGuire (2). We were unsuccessful. Although the Tarver/McGuire model did a good job of predicting temperature of runaway reaction and the approximate time, it could not predict location of the first runaway exotherm. This led us to initiate an effort to develop a better kinetics model. The scheme we used to interpret this data is shown below.

1. HMX (β) $\rightarrow$ HMX (δ)
   (first order endothermic)

2. HMX (β) + HMX (δ) $\rightarrow$ HMX (δ)
   (bimolecular endothermic)

3. HMX (δ) $\rightarrow$ *intermediates*
   (1st order endothermic)

4. HMX (δ) + *intermediates* $\rightarrow$ *final products*
   (bimolecular exothermic)

It is important to realize that this is a global, lumped parameter model that subsumes many important sequential and competing reaction steps. It represents the simplest scheme we were able to develop that accurately describes the thermal traces, and is a refinement of the Tarver/McGuire model. The first two steps, that approximate a nucleation and growth process with an Arrhenius model, are on a relatively firm foundation, with a suite of independent experiments and independently measured rate constants (2). The remaining two steps are on a weaker footing, and require further work. As an empirical model, it is quite effective. When calibrated against the data for one particular experiment, it correctly predicts the temperature, time, and location of ignition

in other experiments, with quite different heating rates, within a few per cent. Nonetheless, we plan to continue experimentation to refine the model and place each set of steps on a solid scientific foundation.

Small Scale Mechanistic Experiments

The small scale experiments described in the previous section were quite good at providing temperature time data, but provided no quantitative data with respect to reaction violence, and no indications regarding the processes occurring after ignition that influence reaction violence. Thus, a separate series of experiments was conducted to obtain direct evidence of post-ignition behaviors. A schematic of these experiments is shown in Figure3.

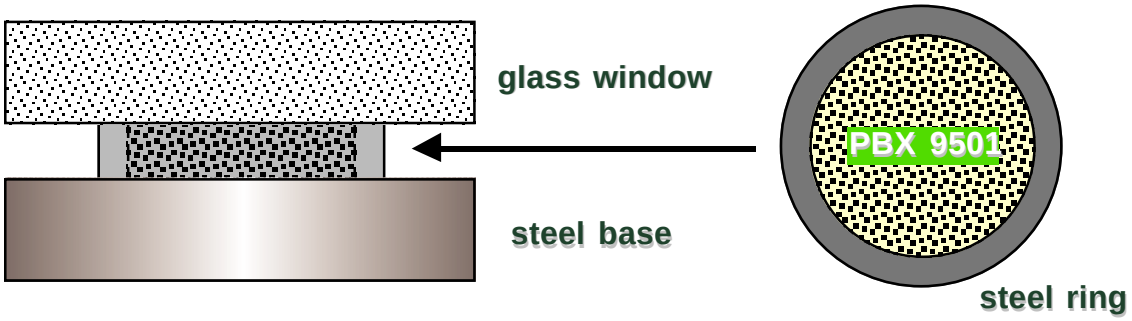

Figure 3: Schematic of small scale mechanistic experiments. Although “steel ring” is indicated, experiments were also conducted with thin copper rings.

The experiments consisted of a thin disc of PBX 9501 axially confined between a toughened glass or sapphire window and a steel heating plate, and radially by a thin ring of steel or copper. Samples were slowly heated to a temperature at which self ignition occurred, or to a prescribed temperature at which ignition was induced by a hot wire. Optical access was provided through the window, and a high speed camera was used to record the events. Figure 4 shows a sequence of photographs resulting from an experiment where deliberate ignition was imposed.

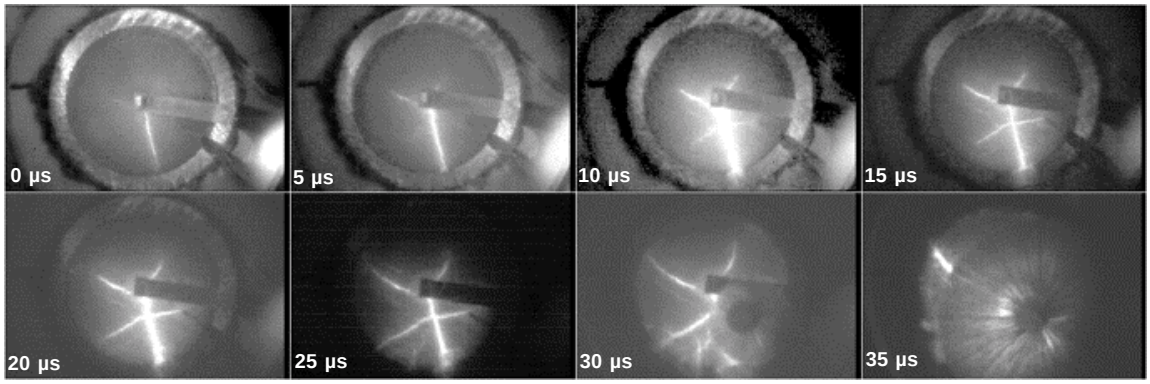

Figure 4: High speed framing sequence for post-ignition behavior of PBX 9501 heated to 190 C and deliberately ignited with a hot wire. Plainly visible is thin copper foil leading to ignition wire. Last two frames show obscuration by fracture of glass window.

The interface temperature between sample and steel plate was 190 C. The photographs show luminous radial cracks emanating from the ignition point. Photographs from a similar experiment are shown in Figure 5. In this case, cracking is much more ramified. The greater ramification is probably a result of observation later in the reaction process. However, uncertainties in assignment of the initial time make this speculative. At any event, it appears quite clear that extensive cracking occurs during the post – ignition process.

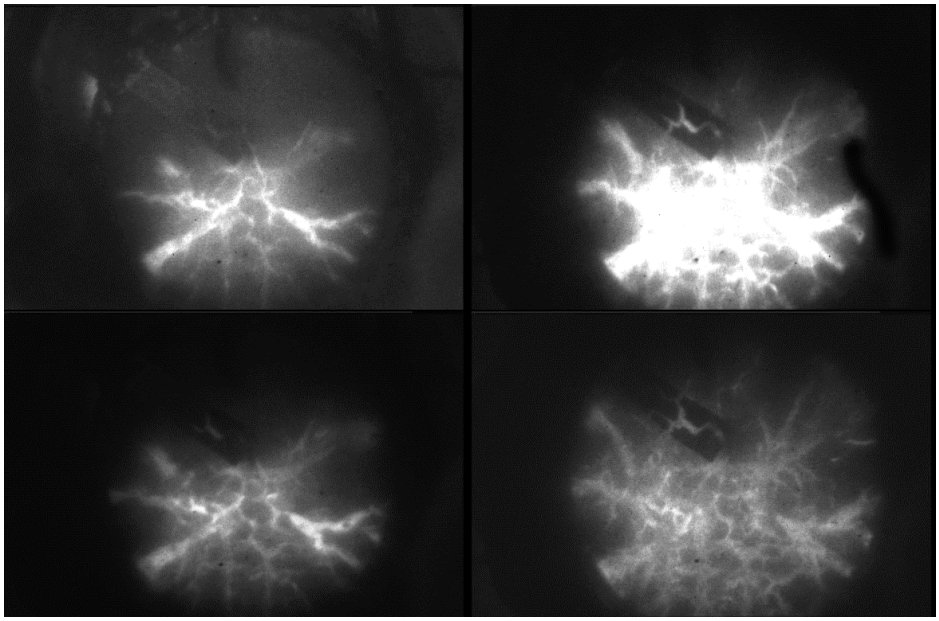
Figure 5: Post - ignition behavior of PBX 9501. Interframe time is five microseconds. Note extensive reactive crack ramification.

The experiments that led to Figure 5 and Figure 6 were both centrally ignited by heating a small nichrome wire. Photographs resulting from an experiment where self-ignition occurred are shown in Figure 6.

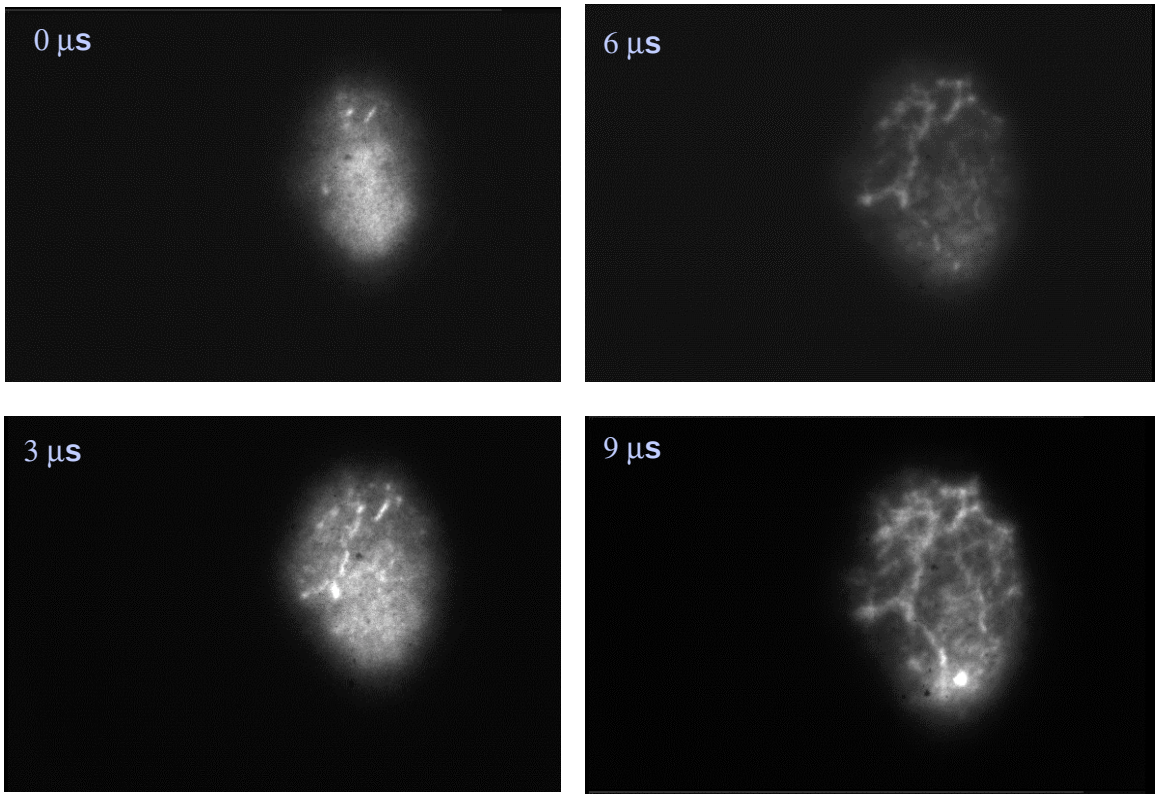

Figure 6: Self ignition of sample of PBX 9501. Sharpness of boundary separating luminous from nonluminous region is an artifact.

The phenomenology is quite similar. In some experiments, there is evidence suggesting that multiple ignitions occur within the time of observation. This would aid in the development of ramified reactive crack networks. We currently believe that nucleation and growth of these reactive crack networks are the primary mechanism by which reaction spreads through the charge after ignition. Whether the reactive cracks are a result of hot gases being pushed down the cracks under conditions of high pressure, or whether the crack tips are causing ignition is a matter of current investigation.

Large Scale Radial Experiments

We conducted some slow cookoff experiments with much larger charge sizes. This was partly to address issues of scaling, and partly for convenience of observation of liner collapse. The experimental configuration is shown in Figure7. The experiments were

instrumented with a suite of thermocouples - typically eighteen placed inside the charge, with six external thermocouples at the boundary - to capture conditions as a function of time. For a complete description of this experiment, see Reference 3. The heating rates for these experiments were extremely low. Extensive care was taken to preserve symmetry of heating.

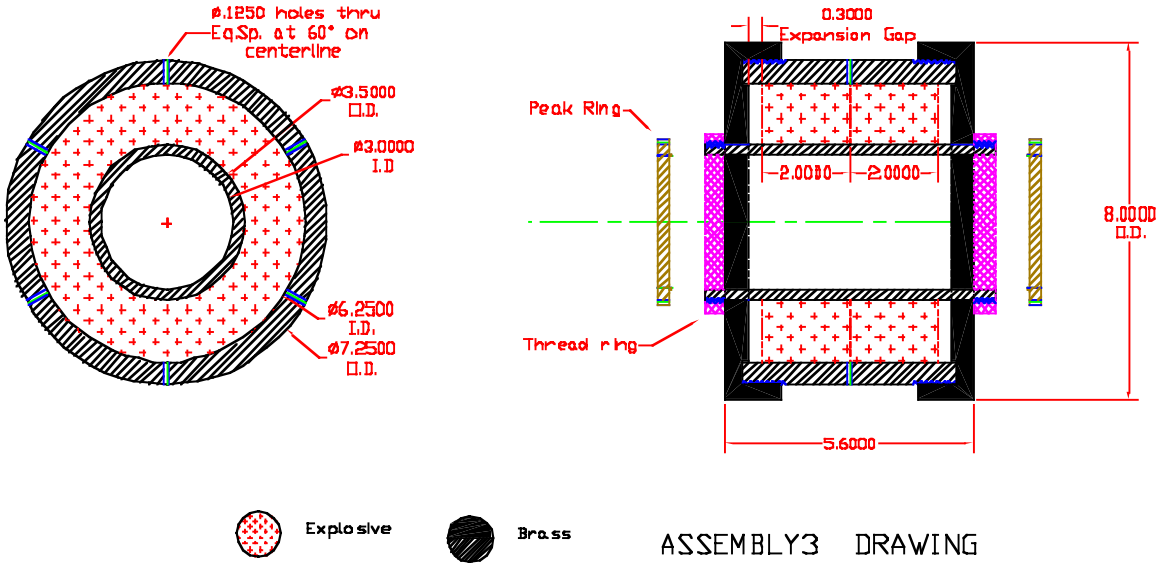

Figure 8: Schematic of large scale experiments. Explosive OD was 6". Eighteen thermocouples were placed at different radial positions in the medial plane of the charge. Both inner and outer cylinders were brass.

Profiles for a set of thermocouples that were located 17.5 mm from the inner explosive – cylinder interface are shown in Figure 8. The experiment was heated to a temperature of about 150C and allowed to equilibrate. This is the plateau apparent in Figure 8. Heating was then continued to bring the explosive through the phase transition and on to the ignition point. Thermocouple measurements at other locations were similar to the set shown here. The heating profiles showed a very high degree of symmetry up until the point at which a runaway reaction occurred. At that time the ignition occurred over a significant portion of the charge. For details, see Reference 3. Apparently, small local material property variations amplified the nonlinearities in the chemical kinetic – heat transfer coupling to cause ignition sites in one region to occur slightly earlier than in other regions. The exact cause of this is of some interest and will receive further work.

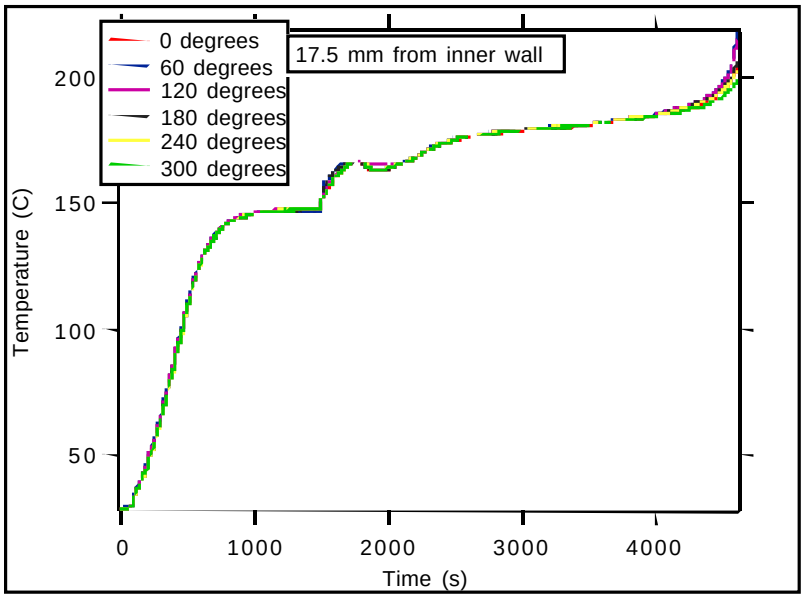

Figure 8: A set of thermocouple traces for thermocouples located 17.5 mm away from the explosive – inner liner interface.

Silhouette pictures of the liner collapse process are shown in Figure 9. These frames show a remarkably high degree of symmetry in the collapse process.

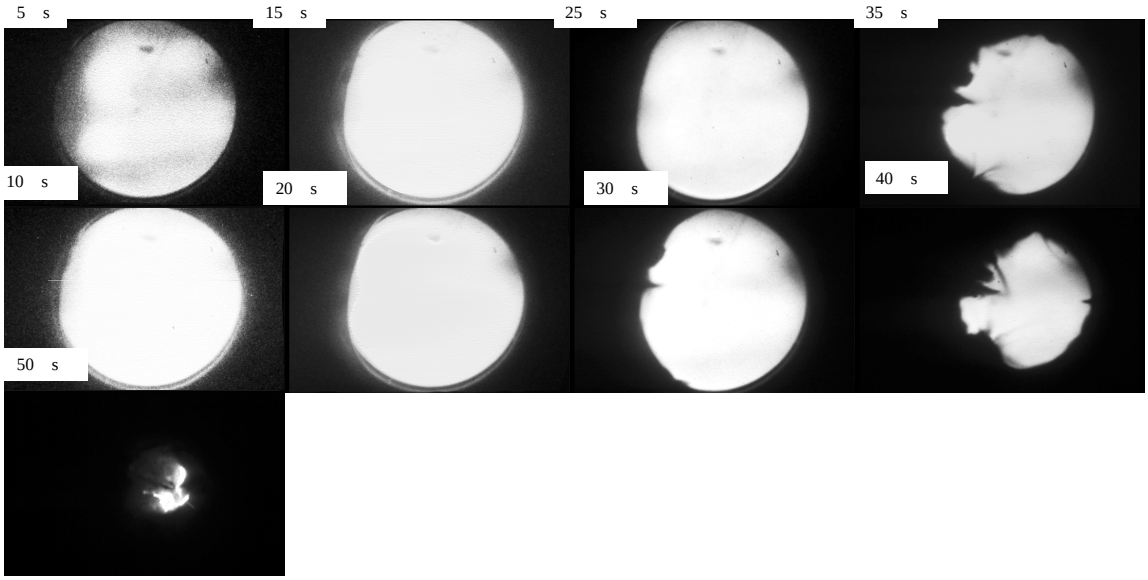

Figure 9: Silhouette pictures of liner collapse in large scale experiment. Sharp projections are caused by explosive product blow by. Interframe times were 5 microseconds.

Discussion and Analysis

Position time measurements made from these frames along a radius extending from the four o'clock position to the axis are shown in Figure 10. The position - time measurements show that the liner collapsed slowly, gaining velocity as it approached the axis. The combination of the gradually increasing collapse speed and the high degree of symmetry suggest a mechanism where a large fraction of the explosive is ignited before much of it can react. This delocalizes the energy release. This is, of course, quite consistent with the nucleation and growth mechanism suggested by the small scale mechanistic experiments described above. It is quite different from what one would expect if a detonation had initiated early in the process, at a single point. Recovered casing fragment size, damage to xray cassettes and test fixtures are consistent with a detonation. It is believed that one or more detonations were initiated in this experiment, but at stages too late to affect the liner collapse process. Other experiments show the presence of initiation of detonation at stages intermediate in the collapse process. In such cases, the symmetry of the collapse process was reduced.

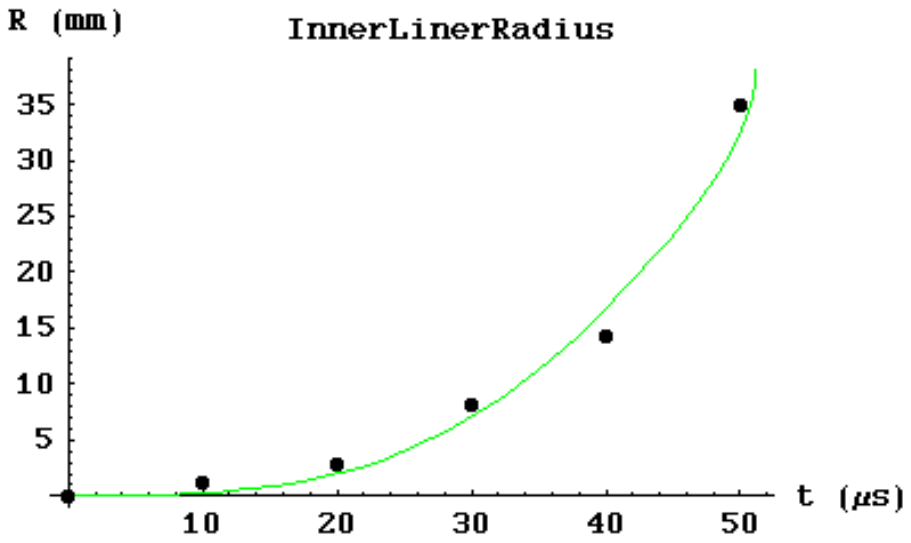

Figure 10: Position – time data inferred from frames in Figure 9. Measurements were made on a radius extending from the four o'clock position to the axis.

The question has been raised as to whether or not the nucleation and crack growth mechanism suggested by the mechanistic experiments can involve enough of the explosive on time scales of interest to produce violent reactions or detonations in cookoff experiments. To address this, we generated a small model that attempted to capture the behaviors and effects of the reactive crack mechanics, without including all the details of the crack formation process. We made the following assumptions for the explosive reaction model:

1. In a uniform temperature field, ignition occurs at large HMX crystals. Once ignition occurs at one or more points, reactive cracks propagate away from the ignition sites.
2. The average crack speed is approximately 500 m/s.
3. The cracks widen as a result of burning. The burning rate was modeled using a fixed burning rate of 20 m/s and as a pressure dependent burning rate taken from the literature. Results were not sensitive to which approach was used here.
4. Cracks bifurcate (or trifurcate) when a certain local energy threshold was exceeded. For example, when a crack penetrated a large HMX crystal (with consequent large amount of energy available for local release upon reaction) the crack was caused to split.
5. A lognormal particle size distribution measured for PBX 9501 was used. Only the largest hundred grains were modeled explicitly.

In addition to the assumptions above, we made the following assumptions to arrive at a simple (but accurate) model for case expansion and liner collapse rate:

1. Neither the explosive nor the casing possessed any material strength.
2. The explosive, when reacting caused a linear velocity gradient to evolve.
3. The solids were incompressible.
4. A constant gamma equation of state was used for the explosive products.
5. Over the lifetime of the calculations, there is no venting, and no gas leakage.

The assumptions are similar to those used in Gurney calculations. Indeed, we extended W. Flis' analysis for our purpose (4).

We used the model to calculate global energy release rates. We incorporated the calculated energy release rates into the equations of motion, and solved them for case expansion rate and liner collapse rate. Since there are numerous arbitrary parameters in the model, we make no claim of predictive capability. Our intent was to examine the hypothesis that a nucleation and reactive crack propagation mechanism could provide the path to violent reactions in cookoff.

We applied the model to the large scale experiments. A set of parametric results is shown in Figures 11 -14. In Figure 11, we show parametric plots of extent of reaction versus time for several different nucleation site densities. The curve with instantaneous energy release is essentially a Gurney calculation – i.e., all the energy was released instantaneously. The curve highlighted in green represents a nucleation and growth rate that matches the position – time data for the large scale experiment described above. Multiple ignition sites were required to generate a sufficiently rapid energy release rate.

The burning that resulted from a crack network emanating from a single nucleation site was generally insufficient to produce energy release rates large enough to match the data.

Figure 12 shows this match and its relation to position – time data calculated using other energy release rates. (Again, the reader is reminded: We aren't claiming predictive capability, we are trying to analyze trends and parameter effects to help us work towards a predictive model.) The liner has reached the axis at a measured time of about 50 microseconds. From Figure 11, we note that the reaction is essentially complete at this time. Although the energy release rate is much, much slower than would result from a detonation, the energy release rate is still fast enough to influence liner collapse.

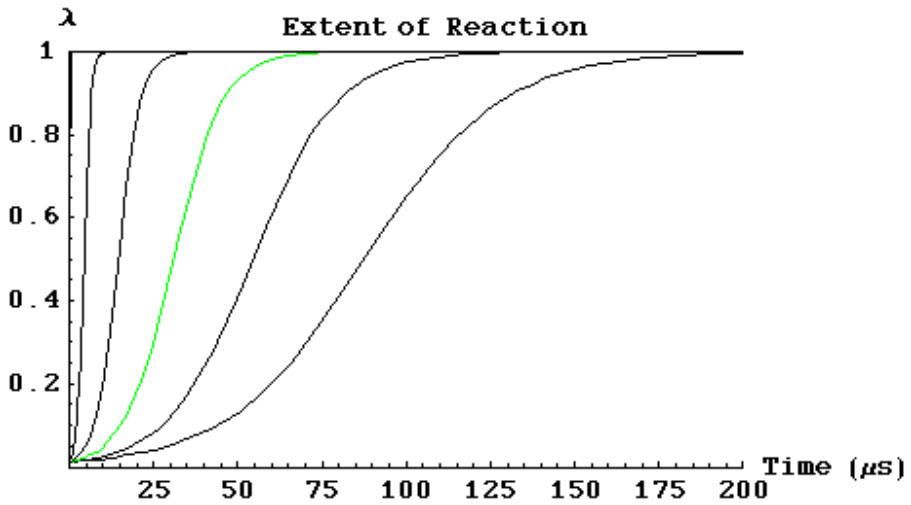

Figure 11: Fraction of energy released as a function of time. Green curve provides good fit to data.

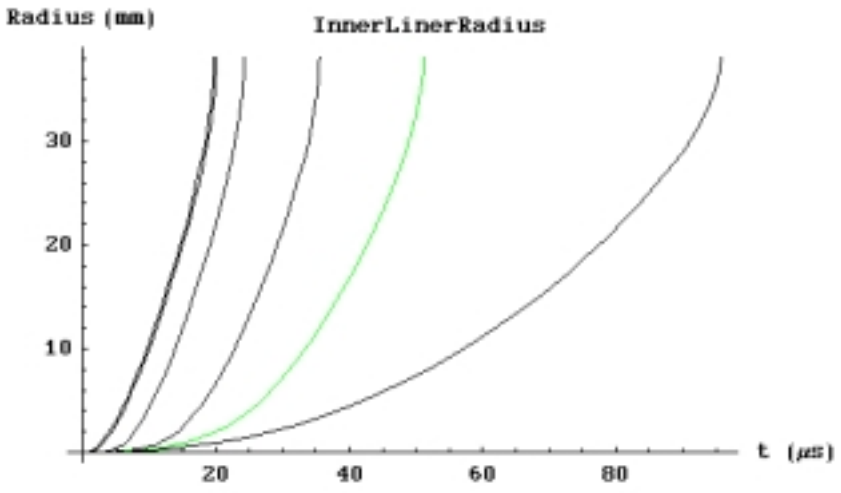

Figure 12: Parametric plots for liner inner surface position versus time for energy release rates shown in Figure 11. Green curve provides good fit to data.

Figure 13 shows a set of parametric calculations for the liner collapse velocity as a function of time. Again, the green curve corresponds to an energy release rate fitted to the data. Initially, the liner collapse rate is much slower than what would be obtained from a detonation. At late times, however, the velocities are commensurate. This is partly due to the nature of the modeled energy release rate, and partly due to the fact that the liner is thickening (causing its inner surface to accelerate) as the liner converges towards the axis.

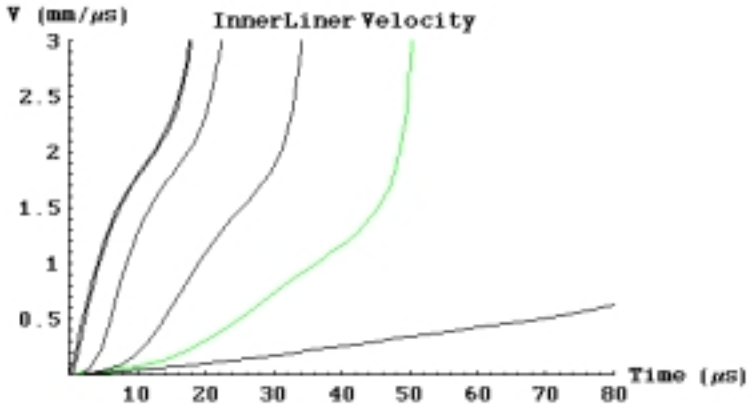

Figure 13: Parametric plots of liner inner surface velocity versus time. Note sharp upswing in velocity as liner approaches axis.

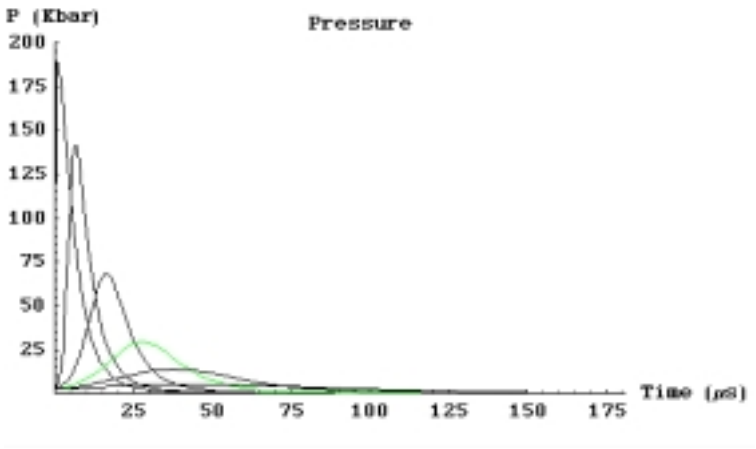

Figure 14: Calculated pressure – time profiles using energy release rates shown in Figure 11. The approximation of a constant gamma gas is probably poor over this region, but the trends are correct.

Calculated pressure histories for the explosive products, based upon a constant gamma gas equation of state, are shown in Figure 14. A gamma value of 3.1 was used. This value was obtained from a calibration of this model against some sandwich test data for PBX 9501 obtained by L. Hill, this laboratory. It is interesting to note that, because of the slow energy release rate and the effect of the case expansion and liner collapse, the calculated peak pressure for the experiment in question is much lower than the peak values for faster energy release rates. Others have reported that case expansion velocities in cookoff experiments can exceed the velocities measured in similar systems that were detonated (5). It may very well be that this is a result of a more gentle pressure loading resulting in a delay in case fragmentation and explosive product blowby, with consequent increased efficiency of t he explosive in accelerating metal.

Conclusion

We are pleased with the progress we are making in addressing this topic. However, we still have a considerable amount of work to do to reach our goal of having a genuinely predictive model. We need additional experiments to bring the chemical kinetics model to maturity and place it on a firm scientific foundation. We need additional experiments that allow us to identify and model quantitatively the processes that occur after ignition. Since reactive crack propagation apparently is important in influencing reaction violence, and since the fracture behavior is intimately coupled with system response, we need to be able to model fracture behavior, the system response, and the coupling between them. This implies a need for good material properties, over the range of thermal environments

of interest. Finally, of course, we will need validation experiments, with an appropriate amount of real system complexity.

We believe that all of this is doable. However, it will require a continued intensive commitment of resources for the next several years. Modern government managers tend to balk at commitments of this sort. However, we believe this is the only approach that promises success. We also believe that placing our understanding of safety issues such as these on a firm scientific foundation is so important that we must follow through.

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